Organometallics **1982**, *1*, 725–732

creased to room temperature. The solution was then poured into 150 mL of pentane and was extracted. Removal of the solvents with a rotary evaporator left ca. 4.0 g of a colorless liquid which was nearly pure **3**. The recovered yield (ca. 60%) was quite low due to the high volatility of peroxide **3**. The peroxide was used without further purification. Attempted purification by column chromatography was unsuccessful as **3** decomposed on silica gel. The spectral properties of **3** are as follows: NMR (CCl_4) δ 0.18 (d, 2 H, J = 2.5 Hz), 1.17 (s, 9 H), 4.58 (heptet, 1 H, J = 2.5 Hz); IR (film) 2980 (s), 2935 (w), 2870 (2), 2140 (s), 1460 (w), 1385 (m), 1365 (s), 1255 (s), 1195 (s), 905 (bd s), 880 (s), 845 (s), 805 (w), 760 (m), 725 cm^{-1} (m); mass spectrum, m/e (% relative intensity) (parent ion not seen), 133 (P^+ − Me, 76), 119 (100), 117 (6), 103 (12), 87 (4), 73 (47), 66 (5), 59 (45), 47 (3).

Thermolysis of Dimethylsilyl *tert*-Butyl Peroxide (3). A 5% solution of **3** in dodecane was prepared and placed in several capillary tubes. After being sealed, these tubes were placed in an oven at 150 °C. The starting peroxide completely disappeared within a half hour. The major products, as observed by GC/MS, were D_4 and silanol **17**. As the initial concentration of **3** in dodecane was increased, the yield of **17** increased.

Reaction of Dimethylsilyl *tert*-Butyl Peroxide (3) with Et_3SiD. Deuteriotriethylsilane was prepared by treatment of triethylchlorosilane with lithium aluminum deuteride in Et_2O. The Et_3SiD was purified by preparative GC (10-ft 15% SE30 column) just prior to use.

To a 5% solution of **3** in octane was added a threefold molar excess of Et_3SiD. This solution was placed in several capillary tubes. After being sealed, the tubes were placed in an oven at 135 °C. The reaction was complete within a half hour. The major products were *tert*-butyl alcohol and 1,1-dimethyl-3,3,3-triethyldisiloxane (**22**). The deuterated alcohol was only identified by GC/MS while **22** was isolated by preparative GC (6-ft. 30% SE column): NMR (CCl_4, 100 MHz) δ 0.16 (d, 6 H, J = 2.5 Hz), 0.35–1.10 (complex multiplet, 15 H), 4.68 (heptet, SiH, 1 H, J = 2.5 Hz); irradiation at δ 4.68 causes the doublet at δ 0.16 to collapse to a singlet; IR (CCl_4) 2965 (s), 2940 (sh), 2920 (m), 2880 (s), 2120 (s), 1465 (m), 1420 (m), 1380 (2), 1250 (bd s), 1065 (bd s), 1000 (s), 910 cm^{-1} (s); the region of Si–D absorption (1520 cm^{-1} for Et_3SiD) is clear; mass spectrum, m/e (% relative intensity) 190 (parent ion, 1), 175 (P^+ − Me, 3), 161 (P^+ − Et, 100), 147 (4), 133 (82), 119 (5), 105 (67), 87 (7), 73 (13), 66 (13), 59 (41).

Reaction of Trimethylsilyl *tert*-Butyl Peroxide (23) with Et_3SiH. A solution containing peroxide **23** (0.0728 g, 0.448 mmol), Et_3SiH (0.188 g, 1.62 mmol), dodecane (0.514 g), and undecane (0.0344 g, GC standard) was prepared. Samples of this solution were placed in capillary tubes which were sealed and placed in an oven at 150 °C. The reaction was complete after 1.5 h. The major products formed were triethylsilanol (17%) and 1,1,1-trimethyltriethyldisiloxane (**24**) (72%). Triethylsilanol was identified by comparison with an authentic sample while **24** was isolated by preparative GC (6-ft 30% SE30 column). The spectral properties of **24** are as follows: NMR (CCl_4) δ 0.08 (s, 9 H), 0.40–1.20 (complex multiplet, 15 H); IR (film) 2980 (s), 2920 (s), 2885 (s), 1460 (m), 1415 (m), 1250 (s), 1240 (sh), 1065 (bd s), 1010 (s), 860 (s), 840 (s), 750 (s), 735 (s), 720 (s), 640 cm^{-1} (w); mass spectrum, m/e (% relative intensity) 204 (parent ion, 1), 189 (P^+ − Me, 6), 175 (P^+ − Et, 100), 161 (9), 147 (80), 133 (12), 119 (75), 117 (13), 105 (15), 103 (12), 87 (11), 80 (9), 73 (39), 66 (28), 59 (36).

Acknowledgment. It is a pleasure to acknowledge the support of this investigation by the National Science Foundation (Grant CHE-8024678) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 3, 78957-19-4; **6**, 31732-54-4; **7**, 80907-02-4; **8**, 80907-03-5; **9**, 80907-04-6; **11**, 80907-05-7; **12**, 80907-06-8; **13**, 80907-07-9; **14**, 10108-37-9; **15**, 80907-08-0; **17**, 80907-09-1; **19**, 17744-86-4; **20**, 80907-10-4; **22**, 80907-11-5; **23**, 3965-63-7; **24**, 2652-41-7; DABCO·2HOO-*t*-Bu, 7216-30-0; di-*tert*-butylbromosilane, 59409-85-7; dimethyl-*tert*-butoxychlorosilane, 58566-07-7; dimethyldichlorosilane, 75-78-5; triethylsilanol, 597-52-4; Et_3SiH, 617-86-7.

Ligand Effects on the Reduction of Iron(III) Complexes by Alkyl Radicals. Formation of Alkyl Isocyanides and Chlorides from Cyanoiron(III) and Chloroiron(III) Species

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The reduction of the cyanoiron(III) complex $(NC)_2Fe(phen)_2^+$ by various alkyl radicals occurs readily by addition to the cyanide ligand to form an alkyl isocyanide coordinated to iron(II). The infrared and electronic spectra of analogous cyanoiron(II) and (alkyl isocyanide)iron(II) complexes are compared in the series: $(CH_3NC)_2Fe(phen)_2^{2+}$, $(CH_3NC)(NC)Fe(phen)_2^+$, $(NC)_2Fe(phen)_2$. Electron-rich alkyl radicals such as *tert*-butyl also reduce $(NC)_2Fe(phen)_2^+$ by an electron-transfer process which affords carbonium ion byproducts. For a particular alkyl radical, the competition between radical addition and electron transfer can be qualitatively related to its ionization potential. Various alkyl radicals also react readily with two series of chloroiron(III) complexes, tetrachloroferrate(III) and trichloroiron(III), to afford the reduced chloroiron(II) species and the corresponding alkyl chloride in essentially quantitative yield. The rates of chlorine atom transfer to alkyl radicals are measured by the competition method using $BrCCl_3$ as a bromine atom donor. The divergent trends in the reactivity pattern of alkyl radicals with tetrachloroferrate(III) and trichloroiron(III) are discussed in terms of $FeCl_4^-$ and $FeCl_2^+$, respectively, as the active chloroiron(III) species in acetonitrile solutions. The various pathways for the reduction of different iron(III) complexes by alkyl radicals are presented in the context of their reduction potentials.

Introduction

Iron is an ubiquitous metal in various biological systems, especially those involving oxidative processes.[1] Coupled with the increasing realization that many oxidative enzymatic processes involve free radical intermediates,[2,3] it is important to delineate the oxidation–reduction reactions

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[1] Ochiai, E. "Bioinorganic Chemistry"; Allyn and Bacon, Inc.: Boston, 1977.

[2] Pryor, W. A., Ed. "Free Radicals in Biology"; Academic Press: New York, 1976–1981; Vols. 1–6.

[3] Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; Chapter 8.

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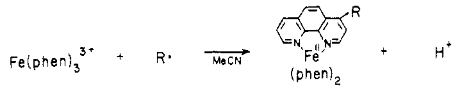
of iron complexes with organic moieties. In the previous study,[4] we identified two major classes of redox reactions which occur between the tris(1,10-phenanthroline) complexes of iron(III) $Fe(phen)_3^{3+}$ and various types of alkyl radicals (R·). The first class of interaction involves an electron transfer to afford carbonium ions (R^+) by an outer-sphere mechanism (eq 1). The second class of interaction results in aromatic substitution specifically at the 4-position of the coordinated phenanthroline by an inner-sphere mechanism (eq 2).[5]

$$Fe(phen)_3^{3+} + R\cdot \xrightarrow[MeCN]{} Fe(phen)_3^{2+} + R^+ \quad (1)$$



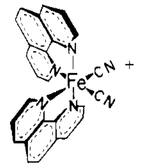
(2)

We now wish to consider a new series of iron(III) complexes I, in which one of the bidentate phenanthroline ligands has been replaced with a pair of anionic ligands, i.e., $X_2Fe(phen)_2^+$, of which the cyano analog (X = CN) is an outstanding example.[6] Such a mixed-ligand complex of $(NC)_2Fe(phen)_2^+$ allows the radical reaction at the cyano ligand to be evaluated directly in competition with the radical attack on the coordinated phenanthroline (as in eq 2) or even electron transfer itself (cf. eq 1). Although the halo derivatives of I are also known, they are unstable in solution with respect to the redistribution of the phenanthroline ligands, e.g., eq 3. Accordingly, we focussed our attention on the radical reaction of two other types of chloroiron(III) complexes, viz., the neutral $FeCl_3$ and the ferrate complex $FeCl_4^-$.

$$3Cl_2Fe(phen)_2^+ \xrightarrow[MeCN]{} 2(phen)_3Fe^{3+} + FeCl_4^- + 2Cl^- \quad (3)$$

Results and Discussion

I. Reduction of the Cyanoiron(III) Complex by Alkyl Radicals. The cyano ligands in the dicyanobis(phenanthroline)iron(III) complex $(NC)_2Fe(phen)_2^+PF_6^-$ are known to be C-coordinated to iron and stable to substitution.[7] The observation of two cyanide stretching frequencies at 2090 and 2077 cm^{-1} coupled with the inequivalency of the two sets of aromatic protons in the pyridino rings of phenanthroline establish the cis configuration,[8] i.e.



The exposure of the dicyanoiron(III) complex $(NC)_2Fe(phen)_2^+$ to methyl radicals in acetonitrile leads to a rapid color change from red to orange, indicative of its reduction to iron(II). [To avoid discontinuity the experimental procedure for the production of methyl and other alkyl radicals is described separately in the Experimental Section.] Pyrolytic gas chromatographic analysis of the crude reaction mixture revealed the presence of methyl isocyanide in at least 60% yields. However, the careful separation of the iron-containing product by column chromatography on silica gel afforded a pure component consisting of the monocyano(methyl isocyanide)bis(phenanthroline)iron(II) cation as the hexafluorophosphate salt, i.e., eq 4. The infrared stretching frequencies of the coordinated cyanide and methyl isocyanide ligands in this cationic complex are listed in Table I. For comparison, the spectral data for the neutral dicyanoiron(II) and the dicationic bis(methyl isocyanide)iron(II) counterparts are also included in the table. The latter was previously prepared by the exhaustive methylation of the dicyanoiron(II) complex with dimethyl sulfate (eq 5).[8,9]

Table I. Spectral Data for Isocyanide and Cyanoiron(II) Complexes

iron(II) complex	infrared ν(CN), cm^{-1}	^{1}H NMR δ (ppm)[c,d]
$(NC)_2Fe(phen)_2$	2090, 2077[a]	
$(NC)(CH_3NC)Fe(phen)_2^+PF_6^-$	2192, 2098[a]	3.48
$(CH_3NC)_2Fe(phen)_2^{2+}2PF_6^-$	2210, 2198[a]	3.47
CH_3NC	2170[b]	3.12

[a] KBr pellet. [b] Neat film. [c] CD_3CN solution. [d] Methyl resonance, phen resonances reported in the Experimental Section.

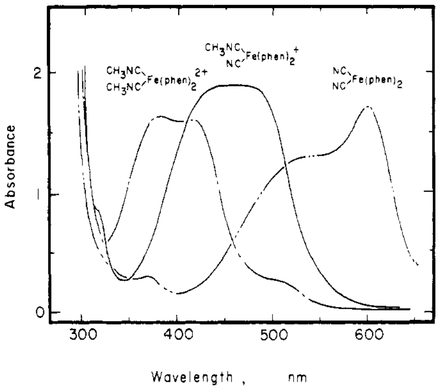
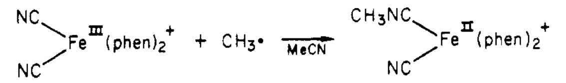
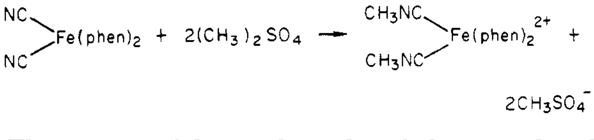


Figure 1. The electronic spectrum of (–··–) 3.72 × 10^{-4} M $(NC)_2Fe(phen)_2$, (—) 3.04 × 10^{-4} M $CH_3NC(NC)Fe(phen)_2PF_6$, and (–·–) 2.90 × 10^{-4} M $(CH_3NC)_2Fe(phen)_2(PF_6)_2$ in methylene chloride solutions.


$$(NC)_2Fe^{III}(phen)_2^+ + CH_3\cdot \xrightarrow[MeCN]{} (CH_3NC)(NC)Fe^{II}(phen)_2^+ \quad (4)$$


$$(NC)_2Fe(phen)_2 + 2(CH_3)_2SO_4 \longrightarrow (CH_3NC)_2Fe(phen)_2^{2+} + 2CH_3SO_4^- \quad (5)$$

The presence of the coordinated methyl isocyanide in both the mono- and di-substituted complexes is also revealed from their ^{1}H NMR spectra which exhibit a single sharp resonance at δ 3.47. The latter is expectedly shifted downfield from that (δ 3.12) of the free methyl isocyanide, as listed in Table I. Furthermore, the inequivalency of the aromatic protons in the terminal rings of the coordinated

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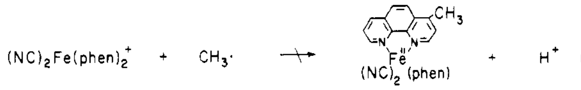
[4] Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *103*, 1319.
[5] See also: Rollick, K. L.; Kochi, J. K. *J. Org. Chem.* **1982**, *47*, 435.
[6] Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000.
[7] See, e.g.: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 113.
[8] Doonan, D. J.; Balch, A. L. *Inorg. Chem.* **1974**, *13*, 921.
[9] Hamer, N. K.; Orgel, L. E. *Nature (London)* **1961**, *190*, 439.

phenanthrolines in the mono(methyl isocyanide) complex supports a cis configuration, similar to those in the dicyano and bis(methyl isocyanide) analogues.[8]

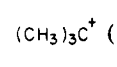
The absorption spectra of these cyano and isocyanide analogues are also compared in Figure 1. For various low-spin iron(II) complexes of the type $X_2Fe(phen)_2$, the electronic spectra are dominated by intense low-energy transitions which have been assigned as metal d to phenanthroline π^* charge transfer.[6] Changes in the nature of X alter the absorption bands mainly by affecting the energies of the filled iron d orbitals.[10] Consequently the systematic variation shown in Figure 1 reflects the increase in the metal → ligand charge-transfer transition upon the successive replacement of a cyano ligand with an isocyanide, which is a better π acceptor and poorer σ donor. Similar changes in spectra have been effected by the treatment of $(NC)_2Fe(phen)_2$ with various Lewis acids.[10]

The methylation of the coordinated cyanide proceeds according to eq 4 in at least 55% yields, as estimated from the integration of the resonance at δ 3.5 in the ^{1}H NMR spectrum of the crude reaction mixture.[11] A further, careful analysis of the ^{1}H NMR spectrum revealed that methylation of the phenanthroline ligand, similar to that in eq 2, did not occur, e.g., eq 6.


(6)

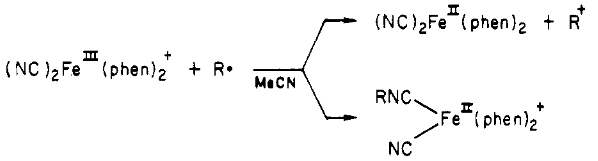
[Previous studies showed that the coordinated methylphenanthroline in iron(II) complexes can be readily identified by its characteristic methyl resonance in the ^{1}H NMR spectrum.[5]] Furthermore, the phenanthroline ligand could be separated from the iron complex in essentially quantitative yield by hydrolytic cleavage (see Experimental Section). Examination of the NMR spectrum of the free phenanthroline fraction revealed no methyl groups indicative of eq 6.

Treatment of the dicyanobis(phenanthroline)iron(III) complex with other alkyl radicals also resulted in the formation of the corresponding alkyl isocyanide complexes by radical addition to the coordinated cyanide. Thus ethyl, isopropyl, and *tert*-butyl radicals afforded ethyl isocyanide, isopropyl isocyanide, and *tert*-butyl isocyanide, respectively, in varying yields upon pyrolytic gas chromatographic analysis of the reaction mixture. These alkyl isocyanides, similar to methyl isocyanide in eq 4, also exist largely as ligands coordinated to iron(II). Thus little if any isocyanide can be separated as the free ligand from the reaction mixture simply by concentration in vacuo. Unfortunately, quantitative analysis of all the organic oxidation products from these alkyl radicals was not achieved for the reason cited above. However, gas chromatographic analysis indicated that other products of alkyl oxidation were formed, especially from *tert*-butyl radicals. Thus in addition to *tert*-butyl isocyanide (~20%), major amounts of isobutylene (30%), *N*-*tert*-butylacetamide (15%), and *tert*-butyl alcohol (30%) were formed. Since the latter are known to arise from *tert*-butyl cations,[4] we conclude that a substantial fraction of the *tert*-butyl radicals was oxidized by $(phen)_2Fe(CN)_2^+$ by a competing electron-transfer process analogous to that in eq 1, viz., eq 7.


(7)

$$(NC)_2Fe^{III}(phen)_2^+ + (CH_3)_3C\cdot \longrightarrow (NC)_2Fe^{II}(phen)_2 + (CH_3)_3C^+ \quad (7)$$

Although isopropyl isocyanide was the major product (~50%), minor amounts of propylene (15%) and *N*-isopropylacetamide (10%) were also formed from isopropyl radical. Similar byproducts (ethylene and *N*-ethylacetamide) from ethyl radical were not detected. Thus the yields of these alkyl byproducts generally increase in the order: methyl, ethyl ≪ isopropyl ≪ *tert*-butyl, at the expense of the corresponding alkyl isocyanide. Such a trend reflects a competition for alkyl radicals between electron transfer and addition in eq 8 and 9, respectively.


(8)
(9)

$$(NC)_2Fe^{III}(phen)_2^+ + R\cdot \xrightarrow[MeCN]{} (NC)_2Fe^{II}(phen)_2 + R^+ \quad (8)$$

$$(NC)_2Fe^{III}(phen)_2^+ + R\cdot \xrightarrow[MeCN]{} (RNC)(NC)Fe^{II}(phen)_2^+ \quad (9)$$

A similar competition was identified earlier in the oxidation of various alkyl radicals and tris(phenanthroline)iron(III), as described by eq 1 and 2.[4] Since electron transfer in eq 1 was shown to be highly dependent on the ease of oxidation of the alkyl radical, it is the dominant pathway with *tert*-butyl radical, but it progressively decreases in importance with isopropyl, ethyl, and methyl radical in accord with the substantial differences in their ionization potentials [$(CH_3)_3C\cdot$, 6.92 eV; $(CH_3)_2CH\cdot$, 7.69 eV; $CH_3CH_2\cdot$, 8.51 eV; $CH_3\cdot$, 9.84 eV[12]]. By contrast, the competing radical addition to a coordinated ligand in eq 2 was not strongly influenced by the ionization potential of the alkyl radical.[5] The overall result is for ligand addition to decrease in the order: methyl > ethyl > isopropyl ≫ *tert*-butyl. Thus we interpret the same trend in the reactions of alkyl radicals with dicyanobis(phenanthroline)iron(III) to reflect a similar competition between electron transfer and ligand addition processes in eq 8 and 9.[13] Furthermore, the strong preference for coordinated alkyl isocyanides to be formed according to eq 9 indicates that radical addition to a cyano ligand is significantly more favorable than addition to phenanthroline as in eq 6.

II. Homolytic Substitution with Chloroiron(III) Complexes.

Two types of chloroiron(III) complexes were employed—the anionic tetrachloroferrate(III) prepared as the tetraethylammonium salt Et_4NFeCl_4 and anhydrous, neutral trichloroiron(III), $FeCl_3$.

A. Tetrachloroferrate(III).

The absorption spectrum of tetraethylammonium tetrachloroferrate(III) in acetonitrile shows two maxima at 312 and 360 nm. Exposure of this pale yellow solution to alkyl radicals affords the corresponding alkyl chlorides in essentially quantitative yields

$$R\cdot + Fe^{III}Cl_4^- \xrightarrow[MeCN]{} RCl + Fe^{II}Cl_3^- \quad (10)$$

where R = methyl, ethyl, isopropyl, and *tert*-butyl. It is noteworthy that *tert*-butyl chloride is formed with no significant admixture of isobutylene.

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(10) Shriver, D. F.; Posner, J. *J. Am. Chem. Soc.* **1966**, *88*, 1672.

(11) Quantitative material balance could not be achieved owing to the partial loss of methyl isocyanide from the complex.

(12) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 4067 and also listing in ref 4.

(13) Two principal mechanisms may be considered for the addition of an alkyl radical to a coordinated cyanide. We favor a one-step process involving a concerted addition. A reviewer has suggested an alternative possibility in which a rate-limiting electron transfer is followed by a rapid cage collapse of the transitory carbonium ion (compare the alkylation in eq 5). Such a two-step process requires that the efficiency of cage collapse varies markedly with alkyl structure in order to account for the result described by eq 8 and 9. We have no direct experimental evidence bearing on this mechanistic distinction at this juncture. However, the facility with which methylation occurs on the cyanoiron(III) complex (as evidenced by the singular absence of attack on solvent) is similar to the methylation of phenanthroline complexes of iron(III) in eq 2, for which there is strong evidence for a concerted addition of the methyl radical to the ligand.[5]

Table II. Rates of Oxidation of Alkyl Radicals by Tetrachloroferrate(III) Relative to Bromine Atom Transfer from Bromotrichloromethane[a]

alkyl radical	ionization potential[b]	source[c]	$k_{Cl}{}^{d}/k_{Br}$	log (k_{Cl}/k_{Br})
methyl	9.84	acetyl peroxide	0.14 ± 0.01	−0.85
ethyl	8.51	Et_4Pb	0.17 ± 0.05	−0.77
		tert-amyl peracetate	0.22 ± 0.05	−0.66
isopropyl	7.69	*i*-PrHgMe	0.19 ± 0.05	−0.72
		2,3-dimethyl-2-butyl peracetate	0.29 ± 0.06	−0.54
tert-butyl	6.92	triptyl peracetate	1.9 ± 0.7	0.28

[a] In acetonitrile at 0 °C under pseudo-first-order conditions. [b] In eV from ref 12. [c] See Experimental Section for methods. [d] See eq 12. Error limits are one standard deviation, at the 95% confidence level, of the relative rates measured.

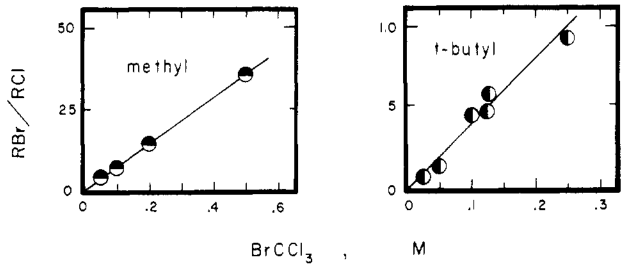

Figure 2. Relative rates of formation of alkyl chlorides from typical alkyl radicals and tetrachloroferrate(III) in competition with bromine atom transfer from bromotrichloromethane.

The rate of homolytic reduction of tetrachloroferrate(III) in eq 10 was measured by the competition method with bromotrichloromethane as the bromine atom donor in eq 11[14] of Scheme I. In the competition experiments, pseudo-first-order conditions were maintained by employing at least a 10-fold excess of $FeCl_4^-$ and $BrCCl_3$. The relative rates of eq 10 and 11 were measured by the relative yields of alkyl chloride and alkyl bromide, i.e., eq 12, as described in the Experimental Section. In order to support the kinetics in Scheme I, the competition was carried out at various molar ratios of $BrCCl_3$ and $FeCl_4^-$, and the ratio of rate constants in eq 12 was obtained from the slopes, typically shown in Figure 2. The ratio of rate constants k_{Cl}/k_{Br} is tabulated for various alkyl radicals in Table II. In each case, the material balance was verified by the trapping of the trichloromethyl radical formed in eq 11 with $FeCl_4^-$, i.e., eq 13. Carbon tetrachloride was indeed isolated in amounts equal to the alkyl bromide, in accord with Scheme I.[15]

Scheme I

$$R\cdot + FeCl_4^- \xrightarrow{k_{Cl}} RCl + FeCl_3^- \qquad (10)$$

$$R\cdot + BrCCl_3 \xrightarrow{k_{Br}} RBr + Cl_3C\cdot \qquad (11)$$

$$\frac{k_{Cl}}{k_{Br}} = \frac{[BrCCl_3][RCl]}{[FeCl_4^-][RBr]} \qquad (12)$$

$$Fe^{III}Cl_4^- + Cl_3C\cdot \rightarrow Fe^{II}Cl_3^- + Cl_4C \qquad (13)$$

B. Trichloroiron(III). The absorption spectrum of $FeCl_3$ in acetonitrile consisted of two bands with maxima at 315 and 360 nm similar to that of the tetrachloroferrate(III). Exposure of an acetonitrile solution of trichloroiron(III) to alkyl radicals afforded excellent yields of the corresponding alkyl chlorides from methyl, ethyl, and isopropyl radicals (eq 14). Since *tert*-butyl chloride was shown to be unstable under these reaction conditions, the primary product(s) could not be ascertained from the reaction of *tert*-butyl radical with trichloroiron(III). Only a mixture of isobutylene and *N*-*tert*-butylacetamide was obtained. [Note that independent studies have established the ready formation of *tert*-butyl cations from *tert*-butyl chloride with $FeCl_3$ in acetonitrile.[16]]

$$R\cdot + Fe^{III}Cl_3 \xrightarrow[MeCN]{} RCl + Fe^{II}Cl_2 \qquad (14)$$

Table III. Rates of Oxidation of Alkyl Radicals by Trichloroiron(III) Relative to Bromine Atom Transfer from Bromotrichloromethane[a]

alkyl radical	source[b]	$k'_{Cl}{}^{c}/k_{Br}$	log k'_{Cl}/k_{Br}
methyl	Me_4Pb	3.6 ± 0.3	0.56
ethyl	Et_4Pb	1.2 ± 0.1	0.08
isopropyl	*i*-Pr_4Sn	1.0 ± 0.1	0.0

[a] In acetonitrile at 0 °C under pseudo-first-order conditions. [b] See Experimental Section for method. [c] See Scheme II. Error limits represent one standard deviation, at the 95% confidence level, of the relative rates measured based on total iron(III).

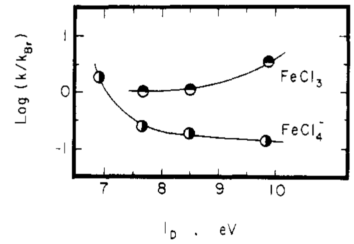

Figure 3. Reactivity pattern for the oxidation of various alkyl radicals by tetrachloroferrate(III) (◑) and trichloroiron(III) (◓) in acetonitrile solution plotted as k_{Cl}/k_{Br} and k'_{Cl}/k_{Br}, respectively, and the ionization potential of the alkyl radical.

The overall rate of the homolytic reduction of trichloroiron(III) in acetonitrile (eq 14) was determined by the same competition method described above for tetrachloroferrate(III) (Scheme II). The ratios of rate constants k'_{Cl}/k_{Br} in Scheme II are listed in Table III for various alkyl radicals.

Scheme II

$$R\cdot + FeCl_3 \xrightarrow{k'_{Cl}} RCl + FeCl_2 \qquad (15)$$

$$R\cdot + BrCCl_3 \xrightarrow{k_{Br}} RBr + Cl_3C\cdot \qquad (16)$$

C. Comparison of Tetrachloroferrate(III) and Trichloroiron(III). The efficient reduction of both tetrachloroferrate(III) and trichloroiron(III) by alkyl radicals is qualitatively reflected in the uniformly high yields of alkyl chlorides which are obtained. Figure 3 compares

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[14] Ingold, K. U. "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 37.

[15] Rollick, K. L. Ph.D. Dissertation, Indiana University.

[16] The synthesis of amides and amidines with *tert*-butyl chloride employs $FeCl_3$ in acetonitrile [Fuks, R. *Tetrahedron* **1973**, *29*, 2147]. Note that *tert*-butyl chloride is stable in the presence of $FeCl_4^-$.

Table IV. Rate Constants for the Reduction of Various Iron(III) Species by Alkyl Radicals Relative to Bromine Atom Transfer from $BrCCl_3$ [a]

iron(III) species	E, V vs. SCE	oxidation process[b]	relative rate constant[c]			
			$CH_3\cdot$	$CH_3CH_2\cdot$	$(CH_3)_2CH\cdot$	$(CH_3)_3C\cdot$
$FeCl_4^-$	−0.08	chlorine transfer (eq 18)[d]	0.14	0.19	0.24	1.9
$FeCl_2(NCMe)_n^+$	0.10	chlorine transfer (eq 19)[d]	3.6	1.2	1.0	
$Fe(phen)_3^{3+}$	0.98	electron transfer (eq 1)[e]	<0.1	0.1	12	36
$Fe(phen)_3^{3+}$	0.98	aromatic substitution (eq 2)[e]	2.2		1	<0.1

[a] In acetonitrile solution. [b] Equations refer to text. [c] Measured with respect to $BrCCl_3$ as donor (k_{Br}), for $FeCl_4^-$ from Table II, for $FeCl_2(NCMe)_n^+$ from Table III, for $Fe(phen)_3^{3+}$ from ref 4. [d] At 0 °C. [e] At 25 °C.

the relative rates of oxidation of these radicals by the two types of chloroiron(III) complexes. Several features are noteworthy in these quantitative comparisons. First, the rates of reduction of trichloroiron(III) are uniformly faster than those of tetrachloroferrate(III) by the same alkyl radical—the factor being more than 25 for methyl radical. Second, tetrachloroferrate(III) and trichloroiron(III) show divergent reactivity patterns for the various alkyl radicals. Thus the relative rates of reduction of tetrachloroferrate(III) increase on proceeding from methyl to ethyl to isopropyl radical, whereas the opposite trend pertains to the reduction of trichloroiron(III). Such differences indicate that different chloroiron(III) species are involved in the reaction of alkyl radicals with tetrachloroferrate(III) and trichloroiron(III) in solution.

A variety of chloroiron(III) species are known to exist in equilibrium with each other, both in aqueous as well as in nonaqueous solutions.[17] Among these, the tetrahedral tetrachloroferrate(III) ion is one of the most stable, and it probably remains intact when Et_4NFeCl_4 is dissolved in acetonitrile.[18] By contrast, there is spectroscopic evidence that the dissolution of trichloroiron(III) in polar aprotic solvents such as dimethylacetamide (S) results in complete ionization according to eq 17.[18] A similar ionization has been suggested to occur in acetonitrile.[19] Cyclic voltammetric studies of tetrachloroferrate(III) and trichloroiron(III) in acetonitrile also support this formulation. Thus tetrachloroferrate(III) shows a single quasi-reversible wave at E = −0.08 V vs. SCE, as shown in Figure 4a. The initial negative scan cyclic voltammogram of an acetonitrile solution of trichloroiron(III) in Figure 4b consists of a pair of partially resolved waves, the first of which occurs at the same potential as that of tetrachloroferrate(III). The second wave, which is displaced to a more positive potential, is consistent with $FeCl_2S_n^+$, since it coincides with the quasi-reversible wave at E = 0.10 V, obtained in the cyclic voltammogram of dichloroiron(II) shown in Figure 4c (S = acetonitrile). Although such an analysis provides a consistent picture of the major chloroiron(III) species extant in solution, it cannot rigorously establish the particular chloroiron(III) species actually involved in the oxidation of an alkyl radical.[20] Nonetheless, let us for the moment assume that $FeCl_4^-$ and $FeCl_2S_n^+$ are indeed the principal chloroiron(III) species responsible for the oxidation of alkyl radicals with tetrachloroferrate(III) and trichloroiron(III), respectively. The opposite trends in

$$2FeCl_3 \xrightarrow[S]{} FeCl_2S_n^+ + FeCl_4^- \qquad (17)$$

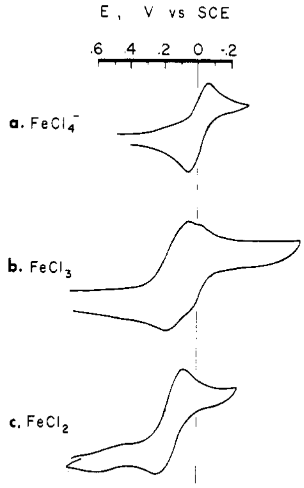

Figure 4. Initial scan cyclic voltammograms of (a) tetraethylammonium tetrachloroferrate(III), (b) trichloroiron(III), and (c) dichloroiron(II) in acetonitrile containing 0.1 M tetraethylammonium perchlorate: sweep rate of 100 mV s^{-1} for a and b and 40 mV s^{-1} for c.

Figure 3 then provide for interesting speculations about different mechanisms of alkyl oxidation. For example, it is possible that $FeCl_4^-$ is reduced by a direct attack of the alkyl radical on the chloro ligand via a bridged activated complex, similar to that presented earlier for a variety of homolytic reactions with metal chlorides,[21] i.e., eq 18. The opposite trend in the behavior of $FeCl_2S_n^+$ may be attributed to an oxidative addition of the alkyl radical to the metal center followed by reductive elimination, i.e., Scheme III. Such a two-step mechanism proceeding via an organoiron(IV) intermediate is akin to that recently presented for the oxidation of methyl radicals by iron porphyrins.[22] Indeed both classes of homolytic mechanisms have been previously elaborated in connection with the oxidations of alkyl radicals by various chlorocopper(II) species.[23] Whether radical attack occurs on the ligand or at the metal, the reduction potential of the complex is an important consideration. Accordingly, let us briefly consider this factor in a broader context.

$$R\cdot + FeCl_4^- \rightarrow [Cl_3Fe\cdots Cl\cdots R]^{\ddagger} \rightarrow FeCl_3^- + RCl \qquad (18)$$

Scheme III

$$FeCl_2S_n^+ + R\cdot \rightarrow RFeCl_2S_n^+ \qquad (19)$$

$$RFeCl_2S_n^+ \rightarrow RCl + FeClS_n^+ \qquad (20)$$

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[17] See, e.g., ref 7, p 753 ff. Benner, L. S.; Root, C. A. *Inorg. Chem.* **1972**, *11*, 652. Work, R. A., III; McDonald, R. L. *Ibid.* **1973**, *12*, 1936. Luter, M. D.; Wertz, D. L. *J. Phys. Chem.* **1981**, *85*, 3543.

[18] Drago, R. S.; Carlson, R. L.; Purcell, K. F. *Inorg. Chem.* **1965**, *4*, 15.

[19] Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry", W. B. Saunders Co.: Philadelphia, 1977; p 235 ff and references therein.

[20] For example, a minor species may be more reactive than a major species.

[21] (a) Kochi, J. K. *Science (Washington, D.C.)* **1967**, *155*, 415. (b) At this juncture, we are unable to define the concertedness of this homolytic process. (c) See: Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 856 for several mechanisms of chlorine atom transfer.

[22] Brault, D.; Neta, P. *J. Am. Chem. Soc.* **1981**, *103*, 2705.

[23] (a) Jenkins, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1972**, *94*, 843 and ref 21c. (b) For equilibria among chlorocuprates(II), see: Smith, D. W. *Coord. Chem. Rev.* **1976**, *21*, 93.

D. Reduction Potentials of Iron(III) Complexes and the Rates of Oxidation of Alkyl Radicals. The competition experiments in Tables II and III provide rate constants for the reduction of the chloroiron(III) species in eq 18 and 19 relative to bromine atom transfer from bromotrichloromethane.[24] These relative rate constants can be compared directly with those obtained in the earlier study[4] of alkyl oxidation by tris(phenanthroline)iron(III) according to eq 1 and 2, since they were carried out under comparable conditions. The relative rate constants for all four processes are relisted in Table IV for convenience. Indeed such a tabulation allows a ready comparison of the reactivity of various alkyl radicals.[25] For example, there is clearly no relationship between reactivity and the reduction potential of the iron(III) species. Next, the trend in reactivity for trichloroiron(III) is closer to that for the inner-sphere aromatic substitution in eq 2 for $Fe(phen)_3^{3+}$ than it is for $FeCl_4^-$, despite the commonality in the chlorine atom transfer in eq 10 and 14. It is also noteworthy that carbonium ion formation with $Fe(phen)_3^{3+}$ in eq 1 shows an unusually steep reactivity pattern, as expected for an outer-sphere electron-transfer process.[26] In order to establish the mechanistic significance of these reactivity patterns, however, further studies of chloroiron(III) species are particularly desirable.

Experimental Section

Materials. Preparation of $(phen)_2Fe(CN)_2ClO_4$. Following the procedure of Schilt,[6] a 0.1 M aqueous solution of $(phen)_3FeSO_4$ (25 mL) was heated until nearly boiling. A fresh solution of KCN (10 g in 10 mL of H_2O) was added all at once, stirred and the solution left to cool. The dark violet crystals were collected and dried in vacuo; yield 4.5 g (90%). A suspension of 2 g of $(phen)_2Fe(CN)_2$ in 200 mL of 1 M HCl was oxidized by bubbling chlorine gas into the hot suspension until a clear, purple solution was obtained. To this was added 4 g of $NaClO_4$ in 50 mL of H_2O, and the product was allowed to crystallize. The product was collected and dried in vacuo at room temperature; yield 2.0 g (91%). **$Fe(H_2O)_6(ClO_4)_3$** was nonyellow reagent grade material from G. F. Smith Co. **$Et_4N\ FeCl_4$.** $FeCl_3{\cdot}6H_2O$ (5.4 g, 0.02 mol) (Mallinckrodt) was dissolved in 95% ethanol. Two milliliters each of concentrated HCl and 30% H_2O_2 were added. After the solution was stirred for 30 min, a concentrated solution of $Et_4N^+Cl^-{\cdot}H_2O$ (Aldrich) in ethanol was added. The mixture was cooled in an ice bath, filtered, and rinsed with ethanol. The collected precipitate was then recrystallized from boiling absolute ethanol and dried in vacuo.[27] **$FeCl_2{\cdot}1.5THF$.**[28] Dry HCl was passed into a flask containing iron powder (Glidden) and 100 mL of anhydrous tetrahydrofuran (THF) at 0 °C with stirring provided by a mechanical stirrer. When all the iron metal disappeared, the HCl was shut off and the precipitate collected by filtration under argon. The product was washed with THF, dried in vacuo at room temperature, and stored under argon. **$FeCl_3$ (anhydrous)** was obtained from Matheson, Coleman and Bell as reagent grade material and used without further purification.

The organometals tetramethyllead, tetraethyllead, tetraethyltin, tetraisopropyltin *tert*-butyltrimethyltin, and related compounds were obtained from previous studies.[26a,29] Acetyl peroxide was prepared following the procedure of Slagle and Shine.[30] The *tert*-alkyl peroxyacetate were prepared as previously described.[23a] **Preparation of Triptyl Peroxyacetate.**[31] Triptyl hydroperoxide (1.32 g, 0.01 mol) was dissolved in 20 mL of pentane, and 0.8 mL (0.01 mol) of freshly distilled acetyl chloride was added. After the solution was cooled to 0 °C, 1 mL of pyridine was added with stirring and the reaction allowed to sit at −20 °C for 4 h. The mixture was poured into cold, dilute HCl. The organic layer was separated and washed with cold, dilute HCl and then with $NaHCO_3$. It was dried over $MgSO_4$ and most of the solvent removed in vacuo. Vacuum distillation yielded 0.98 g (56%) of perester: bp 42–43 °C (0.5 mm); IR[32] 1770 cm^{-1}; NMR δ 2.04 (s, 3 H), 1.27 (s, 6 H), 1.00 (s, 9 H).

Authentic samples of the alkyl isocyanides pertinent to this study were synthesized for comparison. Methyl isocyanide, isopropyl isocyanide, and *tert*-butyl isocyanide were prepared from methylamine, isopropylamine, and *tert*-butylamine, respectively, by using the phase-transfer method of Weber, Gokel, et al.[33] Ethyl isocyanide was prepared from ethyl iodide and silver cyanide.[34]

Reagent grade acetonitrile (Mallinckrodt Chem. Co.) was purified by fractional distillation from calcium hydride. It was stirred with a mixture of $KMnO_4$ and Na_2CO_3, (10 g of each L^{-1}) for 24 h and then filtered. After bulb-to-bulb distillation, it was redistilled from P_2O_5, followed by CaH_2. Acetonitrile obtained in this manner did not reduce $(phen)_3Fe(PF_6)_3$.

Production of Alkyl Radicals for Reaction with Iron(III) Complexes. The various alkyl radicals required for these oxidative studies were generated in acetonitrile solutions independently by two general procedures. For example, alkylmetals spontaneously liberate alkyl radicals upon iron(III) oxidation, as illustrated by the two-step process in Scheme IV for tetraethyltin.[29]

Scheme IV

$$Et_4Sn + Fe^{III} \rightarrow Et_4Sn^{+\cdot} + Fe^{II} \tag{21}$$

$$Et_4Sn^{+\cdot} \xrightarrow{\text{fast}} Et_3Sn^{+} + Et\cdot \tag{22}$$

The subsequent oxidation of alkyl radicals by iron(III) as in eq 1, 2, 8–10, and 14 leads to an overall consumption of 2 equiv of iron(III) for each alkylmetal. General procedures for the use of trichloroiron(III), tetrachloroferrate(III), and dicyanobis(phenanthroline)iron(III) are described below.

Procedure for Trichloroiron(III). A stock solution of trichloroiron(III) in acetonitrile was prepared by dissolving 11 g of anhydrous $FeCl_3$ (Matheson) in 170 mL of dry, oxygen-free acetonitrile. The solution was filtered under argon to remove some insoluble material, and the iron(III) was determined iodometrically. Chloride was determined gravimetrically as silver chloride: found 3.11 $Cl^-/Fe(III)$. A 25-mL flask containing a magnetic stir bar was sealed with a serum cap and flushed with argon for 20 min. Subsequently, 5.00 mL of 0.37 M $FeCl_3$ in CH_3CN, the desired volume of $BrCCl_3$, and sufficient CH_3CN to bring the volume to 9.0 mL were added. The flasks were equilibrated at 0 °C for 30 min, and 1×10^{-4} mol Me_4Pb in 1.00 mL of CH_3CN was added. The reactions were stirred at 0 °C for 10 h and analyzed by gas chromatography on a 10 ft × $^1/_8$ in DBTCP column. **Et_4Pb and i-Pr_4Sn** were treated similarly, but the reaction time was reduced to 2 h. Alkyl halides were analyzed on a 6 ft × $^1/_8$ in. column of FFAP and the olefins on a 10 ft × $^1/_8$ in. column of DBTCP.

Procedure for Tetrachloroferrate(III). A 25-mL flask containing 0.66 g (2.00 mmol) of Et_4NFeCl_4 and a stir bar was sealed with a serum cap and flushed with argon for 20 min. The

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(24) For convenience we continue to assume here that eq 18 and 19 apply to tetrachloroferrate(III) and trichloroiron(III) solutions.

(25) (a) The absolute rate constants k_{Cl} and k'_{Cl} for eq 10 and 15 can be obtained by multiplying the relative rate constants in Table IV by the values of k_{Br}. Unfortunately, k_{Br} has only been evaluated for methyl radicals in the gas phase [$k_{Br} = 6.9 \times 10^5\ M^{-1}\ s^{-1}$ at 65 °C and $2.0 \times 10^5\ M^{-1}\ s^{-1}$ at 0 °C]. Macken, K. V.; Sidebottom, H. W. *Int. J. Chem. Kinet.* **1979**, *11*, 511. For estimates of k_{Br} for other alkyl radicals, see ref 4. (b) The relative rates in each column of Table IV are directly comparable since the value of k_{Br} would be the same.

(26) (a) Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928. (b) The steepness of trend in the relative reactivities is a measure of the sensitivity of iron(III) oxidation to changes in the ionization potential of the alkyl radical. Thus a comparison of the slopes is a meaningful measure of the reactivities of different iron(III) complexes in various alkyl oxidations.

(27) Gill, N. S. *J. Chem. Soc.* **1961**, 3512.

(28) Aresta, M.; Nobile, C. F.; Petruzzelli, D. *Inorg. Chem.* **1977**, *16*, 1817.

(29) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593.

(30) Slagle, J. R.; Shine, H. J. *J. Org. Chem.* **1959**, *24*, 107.

(31) Hedaya, E.; Winstein, S. *J. Am. Chem. Soc.* **1967**, *89*, 1661.

(32) Compare with other peresters. Singer, L. A. In "Organic Peroxides"; Swern, D.; Ed.; Wiley: New York, 1970; Vol. 1, p 273.

(33) Weber, W. P.; Gokel, G. W.; Ugi, I. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 530. Gokel, G. W.; Widera, R. P.; Weber, W. P. *Org. Synth.* **1976**, *55*, 96.

(34) Jackson, H. L.; McKusick, B. C. "Organic Syntheses"; Wiley: New York, 1963; Coll. Vol. 4; p 438.

Table V. Chlorine Atom Transfer from Trichloroiron(III) and Tetrachloroferrate(III) to Alkyl Radicals:[a] Some Typical Examples

				product, μmol			
radical R·	source	$ClFe^{III}$	additive	RH	R (-H)	RCl	RBr
CH_3·	Me_4Pb	$FeCl_3$	0	<0.1		121	0
	Me_4Pb	$FeCl_3$	$BrCCl_3$ [b]			54	77
	perox[c]	$FeCl_4^-$	$BrCCl_3$ [d]			11	42
CH_3CH_2·	Et_4Pb	$FeCl_3$	0	<0.1	<0.1	219	0
	Et_4Pb	$FeCl_4^-$	0	<0.04	<0.04	80	0
	Et_4Pb	$FeCl_4^-$	$BrCCl_3$ [e]	<0.04		13	34
	perox[f]	$FeCl_4^-$	$BrCCl_3$ [e]	<0.04		11	26
$(CH_3)_2CH$·	*i*-Pr_4Sn	$FeCl_3$	0	<0.1	0.7	108	0
	i-PrHgMe	$FeCl_4^-$	$BrCCl_3$ [g]	<0.1		~5	2
	perox[h]	$FeCl_4^-$	$BrCCl_3$ [g]	<0.1		59[i]	10
$(CH_3)_3C$·	perox[j]	$FeCl_4^-$	$BrCCl_3$ [k]		4.5	70[l]	6
	perox[j]	$FeCl_4^-$	$BrCCl_3$ [m]		3.5	30[n]	30

[a] In 10-mL acetonitrile solution with ~2×10^{-3} mol $ClFe^{III}$ and ~1×10^{-4} mol alkylmetal at 0 °C, unless stated otherwise. [b] 0.92 M. [c] 50 μmol of acetyl peroxide. [d] 0.05 M. [e] 0.10 M. [f] *tert*-Amyl peracetate. [g] 0.01 M. [h] 2,3-Dimethyl-2-butyl peracetate. [i] 70 μmol of acetone formed. [j] Triptyl peracetate. [k] 0.02 M. [l] 73 μmol of acetone formed. [m] 0.5 M. [n] 66 μmol of acetone and 33 μmol of CCl_4 formed.

desired volume of $BrCCl_3$ was added, followed by sufficient CH_3CN to bring the volume to 9.0 mL. After equilibration in an ice bath for 30 min, 50 μmol of the organometal in 1.00 mL of CH_3CN was added. The reactions were stirred at 0 °C for 10–24 h and analyzed by gas chromatography using a 6 ft × $^1/_8$ in. column of FFAP for the alkyl halides and a 10 ft × $^1/_8$ in. column of DBTCP for olefins.

The behavior of alkyl radicals generated from organometals (Scheme IV) and those produced from peroxides (Scheme V, vide infra) could not be distinguished in their interaction with either the cyanoiron(III) complex or the chloroiron(III) species (Table V) examined in this study. Furthermore, the kinetic studies carried out under similar conditions on other iron(III) complexes[4,5] support the conclusion that the metal fragment produced in Scheme IV is innocent.

Procedure for Dicyanobis(phenanthroline)iron(III). The iron(III) complex $(NC)_2Fe(phen)_2PF_6$ (0.25 g, 400 μmol) was weighed into a flask which was then sealed with a rubber septum and purged with argon. Acetonitrile (25 mL, O_2 free) was added with the aid of a hypodermic syringe. To this solution was added the organometal (220 μmol) dissolved in 5 mL of acetonitrile. After the solution was stirred for 3 min, the iron complex precipitated; but continued stirring for 8 h resulted in complete dissolution of this material. Gas chromatographic analyses were carried out on a Varian Model 3700 chromatograph using a 30-m glass capillary column of Carbowax 20 M at an injection port temperature of 300 °C and a column temperature of 60 °C for MeNC (4.01 min), EtNC (4.10 min), *i*-PrNC (4.33 min), and *t*-BuNC (4.63 min). The analysis of the alkenes, *N*-alkylacetamides, and alcohols was carried out as previously described.[4] No alkylcyanide was observed with the exception of a small amount of pivalonitrile (~2%) detected from *tert*-butyl radicals. The isomerization of *tert*-butyl isocyanide to pivalonitrile is known to be induced by *tert*-butyl carbonium ions.[35]

The isolation of the isocyanide complex $(CH_3NC)(NC)Fe(phen)_2PF_6$ derived from tetramethyllead was carried out by evaporation of the solvent in vacuo until a solid residue was obtained. A portion of the solid was dissolved in nitromethane, and the mixture chromatographed on a 1 m × 25 mm column packed with 100–200 mesh silica gel which was deactivated by stirring a nitromethane slurry with 10% water. The compound moved through the column as a distinct orange band with nitromethane as the eluant and was isolated as red-orange crystals. It moved as a single spot upon thin-layer chromatography (R_f 0.3). The aromatic region of the ^1H NMR spectrum of $(CH_3NC)(NC)Fe(phen)_2PF_6$ in CD_3CN consisted of multiplets at δ 9.85 (1 H), 9.66 (1 H), 8.73 (2 H), 8.47 (2 H), 8.13 (4 H), 7.99 (2 H), and 7.43 (4 H) relative to the methyl resonance at δ 3.48 (3 H), using nitromethane as the internal standard. Another portion of the solid was dissolved in concentrated H_2SO_4. The solution was then diluted fivefold with water and heated to reflux until colorless. The acidic solution was neutralized with NaOH and warmed until no red color of $(phen)_3Fe^{3+}$ was apparent. It was extracted with methylene chloride, from which phenanthroline could be recovered in essentially quantitative yields. The ^1H NMR spectrum of the recovered phenanthroline fraction in methylene chloride showed no methyl resonance (<1%) at δ 2.3–3.3, indicative of the presence of a methylphenanthroline fraction.[5]

Ethyl, isopropyl, and *tert*-butyl radicals were generated for the reactions with $(NC)_2Fe(phen)_2PF_6$ by a similar procedure from Et_4Pb, *i*-$PrSnMe_3$, and *t*-$BuSnMe_3$, respectively.

The alternative procedure employed for the production of alkyl radicals in the presence of iron(III) complexes involved the catalytic decomposition of peroxides.[36] Thus alkyl radicals can be generated from the iron(II) reduction of peroxides such as the archetypal *tert*-amyl peracetate in Scheme V. Acetone and ethyl radicals were formed in equimolar yields.[15] This procedure is catalytic since the iron(II) species is regenerated during the subsequent oxidation of alkyl radicals by iron(III) (compare eq 1, 2, 10, and 14). The essential mechanism in Scheme V has been discussed in detail for copper catalysis.[37] As applied to tetrachloroferrate(III), the reaction flask containing 2.00 mmol of Et_4NFeCl_4 was treated with 8 mL of acetonitrile. A solution of the peroxide in acetonitrile was prepared under argon at 0 °C, and 1.00 mL was added to the flask at 0 °C with the aid of a hypodermic syringe with a platinum needle. A 1.00-mL aliquot of CH_3CN containing 1×10^{-6} mol of $FeCl_2 \cdot 1.5THF$ was added, and the reactions stirred at 0 °C for 2–3 h. Analyses were carried out as described above.

Scheme V

$$AcOOC(CH_3)_2Et + Fe^{II} \rightarrow AcOFe^{III} + Et(CH_3)_2CO\cdot \quad (23)$$

$$Et(CH_3)_2CO\cdot \xrightarrow{\text{fast}} (CH_3)_2CO + Et\cdot \quad (24)$$

Oxidation of Ethyl Radicals by Aquoiron(III) Species. Ethyl radical derived from oxidation of tetraethyllead by $Fe(H_2O)_6(ClO_4)_3$ in acetonitrile afforded a mixture of products including ethylene, ethanol, and *N*-ethylacetamide. As shown in Table VI, the yield of ethanol increased, at the expense of the ethylene and *N*-ethylacetamide, upon the dilution of acetonitrile with water. A maximum of 25% water (vol %) was added, owing to the limited solubility of Et_4Pb.

The experiments were carried out with nonyellow $[Fe(H_2O)_6](ClO_4)_3$ (1.84 g, 4.00 mmol) (G. F. Smith) placed in a 25-mL flask with a magnetic stir bar. The flask was sealed with a serum cap and flushed with argon for 20 min. The desired volume of degassed, distilled water and sufficient CH_3CN to bring the volume to 15 mL were added. Subsequently, 200 μL (1.0 mmol) of Et_4Pb was added, and the reaction was stirred at room temperature for

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(35) Saegusa, T.; Takaishi, N.; Ito, Y. *J. Org. Chem.* **1969**, *34*, 4040.

(36) Cf. Sosnovsky, G.; Rawlinson, D. J. "Organic Peroxides"; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1, Chapter 10.

(37) Kochi, J. K. *Tetrahedron* **1962**, *18*, 483. Kochi, J. K.; Bemis, A. *Ibid.* **1968**, *24*, 5099.

Table VI. Oxidation of Ethyl Radical by $Fe^{3+}(aq)$ in Acetonitrile-Water Mixtures[a]

H_2O[b]	ethyl products, mmol			
	EtH	Et (-H)	EtOH	EtNHAc
0	0.16	0.09	0.51	0.30
10	0.55	0.04	0.71	trace[c]
25[d]	0.41	0.01	0.80	trace[c]

[a] Reactions carried out with 4.0 mmol of $Fe(H_2O)_6(ClO_4)_3$ and 1.0 mmol of Et_4Pb in 15 mL of solvent at 22 °C. [b] Volume %. [c] $\leqslant 0.05$ mmol. [d] Et_4Pb not completely dissolved.

8 h. Ethane and ethylene were determined by gas chromatography using a 2 ft × $^1/_8$ in. column of Porapak Q. Ethanol was analyzed on a 6 ft × $^1/_8$ in. column of Porapak Q. A 3 ft × $^1/_8$ in. column of FFAP was used for the analysis of *N*-ethylacetamide.

The results in Table VI indicate that ethyl radicals are readily oxidized by iron(III) in either acetonitrile or aqueous acetonitrile solutions to afford high yields of *N*-ethylacetamide and/or ethyl alcohol. Such an oxidation can proceed by either electron transfer to afford an ethyl cation or by an associative process involving an ethyliron(IV) intermediate.[38] These mechanisms bear critically on other oxidations such as those utilizing the Fenton's reagent[39] and merit further study.

Acknowledgment. We wish to thank the National Science Foundation for financial support and W. Lau for help with the spectral measurements.

Registry No. $(NC)_2Fe(phen)_2$, 15362-08-0; $CH_3NC(NC)Fe(phen)_2PF_6$, 80925-96-8; $(CH_3NC)_2Fe(phen)_2(PF_6)_2$, 49664-77-9; CH_3NC, 75-05-8; $(NC)_2Fe(phen)_2PF_6$, 80925-97-9; $Fe(H_2O)_6(ClO_4)_3$, 32963-81-8; $FeCl_4^-$, 14946-92-0; $FeCl_3$, 7705-08-0; $FeCl_2$, 7758-94-3; $FeCl_2^+$, 15905-98-3; $CH_3\cdot$, 2229-07-4; $CH_3CH_2\cdot$, 2025-56-1; $(CH_3)_2CH\cdot$, 2025-55-0; $(CH_3)3C\cdot$, 14804-25-2.

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(38) At this juncture, the source of the increasing yields of ethane with water concentration is somewhat ambiguous. A reviewer has indicated that Et_4Pb does not undergo unassisted hydrolysis by water at any appreciable rate. However, the formation of ethyl alcohol and *N*-ethylacetamide does generate an equivalent of acid, which could lead to an enhanced rate of protonolysis. Alternatively, ethane may arise from the hydrolysis of a putative organoiron intermediate; as suggested by the reviewer.

(39) Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.

Cyclopentadienylcobalt 1,4-Diaryltetraazadienes. A Structural, Spectroscopic, and Theoretical Study

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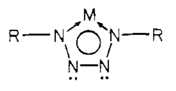
Unsaturated metallacycles such as $(\eta^5\text{-}C_5H_5)Co(R{-}N{=}N{-}N{=}N{-}R)$, where R = alkyl or aryl, offer the possibility of π-delocalized bonding. $X\alpha$ calculations predict that two $d\pi$ electrons on the $(\eta^5\text{-}C_5H_5)Co$ fragment should strongly interact with an empty low-lying π^* orbital of the tetraazadiene ligand to yield metallacycle π and π^* orbitals. A single-crystal X-ray diffraction study at −150 °C of the R = C_6F_5 derivative provides direct evidence of the π-acceptor abilities of the RN_4R ligand. The $Co[(\overline{N(1)N(2)N(3)N(4)})]$ ring is planar and exhibits unusually short Co–N(1) and Co–N(4) distances of 1.802 (2) and 1.819 (2) Å, respectively, indicative of multiple-bond character. The short N(2)–N(3) bond [1.279 (2) Å] and long N(1)–N(2) [1.360 (2) Å] and N(3)–N(4) [1.355 (2) Å] bonds demonstrate that π back-bonding has altered the pattern of unsaturated bonds in the tetraazadiene chelate. Electronic absorption spectra of $(\eta^5\text{-}C_5H_5)Co(RN_4R)$ [R = CH_3, C_6H_5, C_6F_5, 2,4-$F_2C_6H_3$, 2,6-$(CH_3)_2C_6H_3$] display three bands characteristic of the cobalt–tetraazadiene ring: $\lambda_{max}{}^1$ (ϵ), 600–670 nm (300–700); $\lambda_{max}{}^2$ (ϵ), 425–470 nm (5000–9000); $\lambda_{max}{}^3$ (ϵ), 335–390 nm (<4000). These absorptions are attributed to one-electron transitions that terminate in the low-lying metallacycle π^* orbital. Crystals of $C_{17}H_5CoF_{10}N_4\cdot{}^1/_2C_6H_6$ at −150 °C are monoclinic, space group $P2_1/c$, with four formula units in a cell of dimensions $a = 8.612$ (4) Å, $b = 22.687$ (12) Å, $c = 9.820$ (6) Å, and $\beta = 91.58$ (2)°. Least-squares refinement of 315 variables has led to a final value of the R index on F^2 of 0.047 for 5367 observations; the conventional R index on F is 0.033 for 4313 observations having $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Partially occupied π orbitals on a metal atom and unsaturated chelate permit the formulation of a $(4n + 2)$ π-electron ring. Six electron systems such as I, where M is $(\eta^5\text{-}C_5H_5)Co$, $Fe(CO)_3$, or some other d^8 moiety have attracted our attention.[1,2] The available structural data for metallacyclopentadiene complexes, MC_4R_4 (II), indicate little delocalization of the π-electron system;[3] extended Hückel molecular orbital calculations support these observations.[4] Delocalized electronic structures have been proposed for heterocycles of the type $MC_2R_2X_2$, X = S, NR′ (III), on the basis of structure determinations and spectroscopic data.[5,6] Further heteroatom substitution



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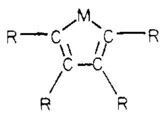

II

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